ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN: 1584 - 2673

RESEARCHES CONCERNING TO THE POSSIBILITY OF USE THE SIDERITIC RESIDUE FOR PRODUCTION OF CLINKER

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ABSTRACT:
The work presents some researches regarding to utilization in cement industry of the sideritic residue, stored in the ponds near from Hunedoara. Thus, on the chemical and granulometric compositions is obtained a number of 10 recipes of clinker, and finally are presented an optimum recipe. The purpose of this researches was reused a manufactured residue, which momentary is stored on large ground surfaces. Through suggested variant are desired the rendition to natural area of this polluted surfaces, parallel with economic effect for reducing quantities of calcite and clay in clinkers production from the cement industry.
Keywords: Sideritic residue, clinker production, cement, polluted surface, recycling

1. INTRODUCTION

The metallurgical industry represents a strong source of environment pollution related through the amounts of gas and dust emanates in atmosphere and the through residues quantities stored in ponds on dumps.

In this the sense the iron ore the type siderite with ferric contents of 25-40% and roasted in the sight of carbon oxide eliminate, what causes concentration of iron ore and transformation of mineral from carbonate in iron oxide with magnetic property. Behind of magnetic concentration operations, in result concentrate the iron arrives at concentration of 51-53%, can be used in agglomeration process, and sterile is stored in ponds.

Suchlike this technological process it was at ore preparation plan of Teliuc- Hunedoara, within 1998 when the primary elaboration steel flux (coke plant - Siemens-Martin steelwork) from S.C. Siderurgica S.A it was complete deallocated. In afferent ponds ore preparation plan of Teliuc-Hunedoara it was remained stored in ponds huge quantities of siderite sterile (cca 12 mil. tons). Sterile can be submitted to a concentration operations, and resulted sterile (secondary sterile) can be used-up as the correction addition for obtains of clinker (the chemical composition permits this thing).

2. THE STUDY

In order to be determined the quantities of the waste materials deposited into the ponds within Hunedoara aria the topographic measurements have been performed in the system of 1970`s stereographic coordinates and for reference system of Black Sea quotes. In the fig. 1 it is presenting the design of framing in the aria of the studied emplacements. The fig.2 presents the framing design in the aria of 1 Pond, respectively the fig. 3 for the 2-nd and the 3-rd Ponds [3].

The data obtained by measurements were worked in AUTOCAD adding program resulting the situational plans from which is caused the amounts of existing residues.

Analyzing the measurements and situational plans obtained for the objective taken under consideration results the next amounts of stored residues:

- Sludge bed no.1 – Teliuc excavation: the sludge bed deals a surface of 25 hectare, the amount of residues (sideritic concentrate) 7 million tons.
- Sludge bed no.2 – Teliuc excavation: the sludge bed deals a surface of 18 hectare, the amount of residues (sideritic concentrate) 5 million tons.
- Sludge bed no.3 – Teliuc excavation: the sludge bed deals a surface of 32 hectare, the amount of residues (sideritic concentrate) 9 million tons

Figure 1. The integration plan in studious emplacement zone.

Figure 2. The integration plan in sludge bed no.1 Teliuc area.

Figure 3. The integration plan in sludge bed no.2 and 3, Teliuc area

The sideritic residue chemical composition (the 10 proofs taken and average value) is presented in table 1 and the chart, in figure 4.

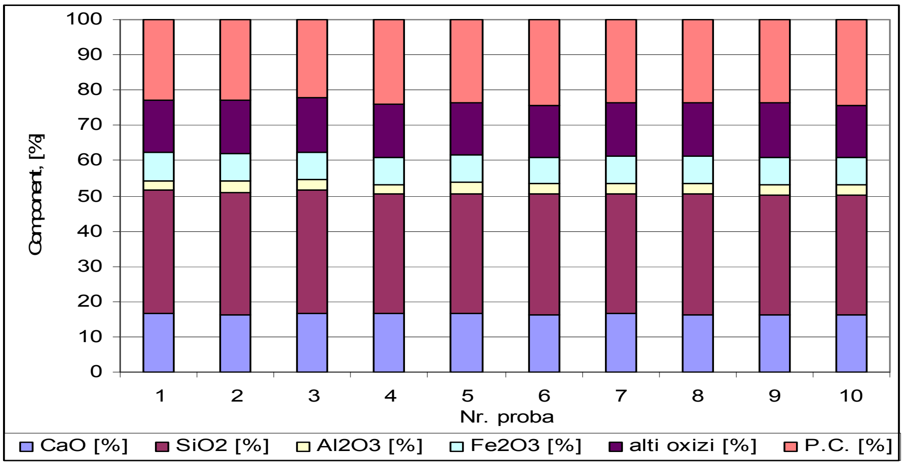

Figure 4. Taken samples chemical composition

Table 1. The sideritic residue chemical composition from sludge beds, [%]

The sideritic residue from sludge beds	CaO	SiO_2	Al_2O_3	Fe_2O_3	Others component	P.C.
1	16,54	35,02	2,84	7,8	14,98	22,82
2	16,27	34,8	3,04	7,94	15,22	22,73
3	16,59	34,91	3	8,04	15,46	22
4	16,55	33,89	2,68	7,8	15,01	24,07
5	16,48	34,22	3,07	7,9	14,63	23,7
6	16,34	34,25	2,88	7,54	14,75	24,24
7	16,44	34,28	2,75	7,85	15,21	23,47
8	16,4	34,19	2,81	8,01	14,95	23,64
9	16,22	34,1	2,85	7,88	15,15	23,8
10	16,07	34,24	2,78	7,64	15,04	24,23
Average	16,39	34,39	2,87	7,84	15,04	23,47

We experimented a number of 10 recipes with component presented in table 2; the chemical composition of the recipes with and without the loss to calcinations it presented in figure 5 and 6 [3].

Table 2. Recipes component, [%]

Component	Recipe no.									
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
Calcite	72	72	75	73	74	74	75	75	76	76
Clay	14	15	13	14	13	14	12	13	12	13
Sideritic residue	14	13	12	13	13	12	13	12	12	11
Total	100	100	100	100	100	100	100	100	100	100

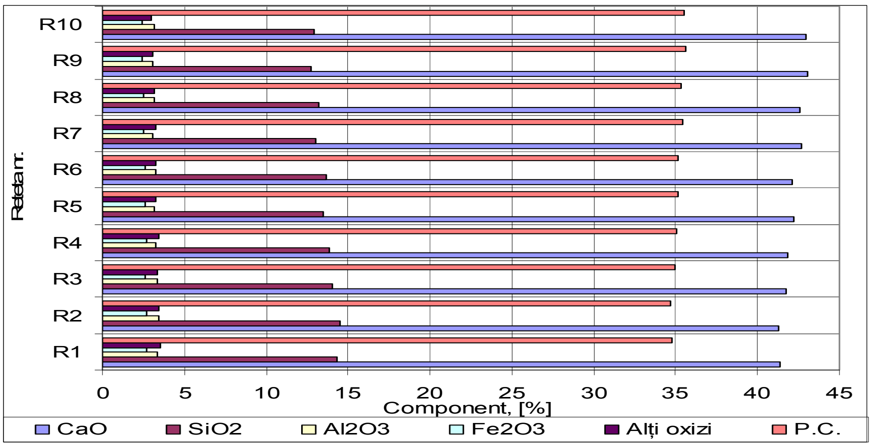

Figure 5. Chemical compositions of started recipes

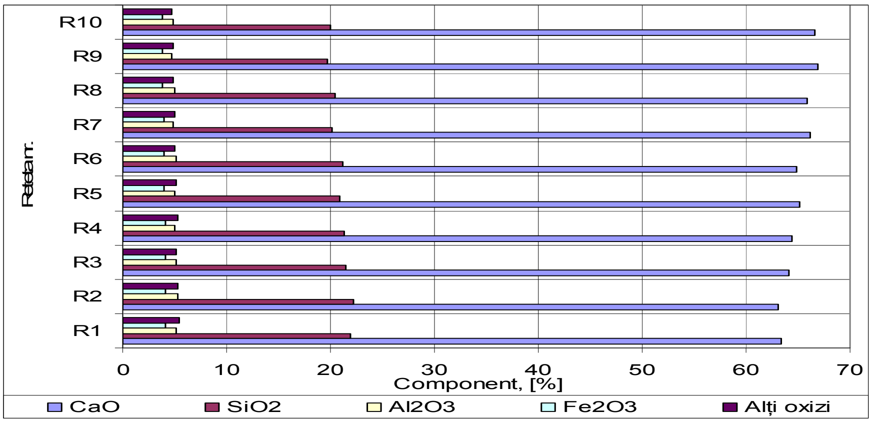

Figure 6. Chemicals composition of recipes without losses by calcinations

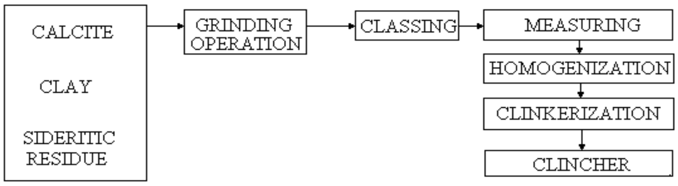

Figure 7. The raw materials worked technological flux in order to obtained clinker

The raw materials was worked, base of the technological flux presented in fig. 7. The crushing (the clay and the limestone came in bunches), we used a ball mill, existing the Metallic Smelting Laboratory. After crushing (the resulting grain size being below 250µm), the materials were graded in the laboratory installation, dosed, by means of analytical scales and homogenized in a homogenizing drum. Fig. 8 shows aspects of these experiments.

Figure 8. The installations used for clinker production

After the recipes have been obtained, the materials were clinkerized in a Tamman resistance furnace, each sample weighing 200g. The resulting samples showed a degree of reduction ranging between 30-42,5%.

3. ANALISES, DISCUSIONS, APPROACHES, INTERPRETATIONS

The Portland clinker represents the product obtained by calcinations till to the partial smelting, of a homogenous mixture, fine crushing, of the calcareous and as clay raw materials, and, eventually, different for correction additions. In the technology of the Portland cement manufacturing, the clinker represents a semi-finished product.

The clinker chemical composition of Portland cement represents the percentage content shown in the chemical elements, computed as oxides. The chemical composition is expressed in oxides because the chemical transformations ,which the raw materials are suffering during the clinkering, do not involve the destruction of the liaisons between the respective elements and Oxygen, so, in the new formed constituted elements, the oxides are coming into as the molar well constituted units.

The clinker characterization, from the oxides composition point of view, can be made using the ***modules***. The modular system is based on the co-relations that are established between the oxidic composition and mineralogical one, of the clinkers, simplifying by this the computation of the gross mixture and deduction of some characteristics of the cements will follow to be manufactured [1]. The main modules used in there cement industry are: the module of silica, module of alumina and grade of saturation in calce.

The module of silica (M_{Si}) represents the ration between the percentage content of SiO_2 and percentage content of $Al_2O_3+Fe_2O_3$ from the clinker.

$$M_{Si} = \frac{\%SiO_2}{\%Al_2O_3 + \%Fe_2O_3} \quad (1)$$

The clinkers of Portland cement have, normally, M_{Si}=1,5...4. The silica module value is given the information regarding mineralogical composition of the clinker, respectively upon the content of silicates and aluminates: $(C_3S+C_2S)/(C_3A+C_4AF)$, as well as upon the conduct of the gross mixture on burning, regarding the content into the liquid phase (the silicates remained into the solid phase, and in the meantime aluminates, merely ferrite-aluminates passed into the liquid phase). In case of a high module of silica, the clinkering is realized in more difficult conditions; for the values of silica module higher than 2.5 the clinkering is made harder, with a great consumption of energy; for M_{Si} =2...2,5 the clinkering is going normally, and for M_{Si} lower than 2, the clinkering is making easy. The clinkers with M_{Si} lower than 1,5 give the cements with very speedy connection/bind.

The module of alumina (M_{Al}) is the ration between the percentage content of Al_2O_3 and Fe_2O_3 of the clinker:

$$M_{Al} = \frac{\%Al_2O_3}{\%Fe_2O_3} \quad (2)$$

For the common clinkers, the module of alumina has the values comprised between 0.2 and 5. Its value gives the information regarding the percentage of aluminates phases. Ferrite and ferrite-aluminates phases from the clinker:

- at M_{Al} higher than 0.64, all quantity of Fe_2O_3 appears as binded in ferrite-aluminate solid solution, the over plus of de Al_2O_3 is forming C_3A;
- la M_{Al} lower than 0.64, all quantity of Al_2O_3 appears as binded in ferrite-aluminate solid solution, the over plus of Fe_2O_3 is forming C_2F;
- M_{Al}=0.64, all quantity of Al_2O_3 and Fe_2O_3 is binded with CaO as C_4AF [2].

The degree of saturation in calce (S_K) represents the ration between the percentage content of CaO that exists in the clinker and the quantity of CaO that is necessary for the saturation of SiO_2, Al_2O_3 and Fe_2O_3 at the mineralogical constituted elements that are characteristically to the clinker, with the condition that CaO to not remain un-binded (free):

$$S_K = \frac{\%CaO}{2,8\%SiO_2 + 1,1\%Al_2O_3 + 0,7\%Fe_2O_3} \quad (3)$$

Table 3. Oxides chemical composition of raw materials

Raw materials	Oxides chemical composition of raw materials, [%]					
	CaO	SiO_2	Al_2O_3	Fe_2O_3	Others oxides	Losses by calcinations
Calcite	53,2	3,0	1,5	1,0	0,5	41,8
Clay	5,51	52,56	13,21	6,32	7,44	14,96
Sideritic residue	16,39	34,39	2,87	7,84	15,04	23,47

The standard calce (K_S) is used to us, also, that coincides with the formulation given by German scholarly Kühl for the saturation grade in calce, but the value S_K will be multiply with 100.

In order to obtain in the laboratory a clinker of the cement there were used as the raw materials the calcareous stone and clay from CARPATCEMENT HOLDING – Deva factory and sideritic waste material from Teliuc pond. The chemical composition of these raw materials is given in the table 3.

Based on the composition of the clinker obtained at CARPATCEMENT HOLDING SA – Deva Factory, the computations have been done for the determination of the percentage composition of the gross mixture formed by calcareous stone, clay and sideritic waste material and which from must result a clinker that will follow to have S_K=0.98 and M_{Si} = 2.34. We made modular calculus for all blends of raw matters; the results are presented in table 4.

Table 4. Blends of raw materials for clinker production

No. proof	Blend compositions, [%]			Modular compositions	
	Calcite	Clay	Sideritic residue	S_K	M_{Si}
1	72	14	14	0,905	2,376
2	72	15	13	0,893	2,371
3	75	13	12	1,012	2,318
4	73	14	13	0,932	2,355
5	**74**	**13**	**13**	**0,98**	**2,34**
6	74	14	12	0,961	2,335
7	75	12	13	1,025	2,322
8	75	13	12	1,008	2,318
9	76	12	12	1,058	2,300
10	76	13	11	1,04	2,296

4. CONCLUSIONES

There can be observed that the optimum mixture is from the **sample 5**, because at the samples 3, 7, 8, 9 and 10 (to which the percentage of calcareous stone is more than 74%), the grade of saturation in calce has a value higher than 1, and it means that from the mixture of the raw materials, after clinkering, will remain free CaO that is damaging the quality of the clinker. At the samples 1, 2, 4, and 6, the value of the saturation grade into the calce is lower than that one of the clinker we like to obtain.

Referring to the values of the silica module, there can be observed that they do not present significant variations for the samples are analyzed. So, in order to obtain an adequate clinker, the blend of raw matters must content the follow: 74% calcite; 13% clay; 13% sideritic residue. The analysis of the results has lead to the following conclusions:

- the process has a low economical efficiency, as this solution requires a further clinkering process and replaces only partially some quantities of clay and limestone by sideritic waste;
- considering the actual economical context, we are looking for solutions meant to reduce the amount of clinker used in cement production, which have direct implications on its cost, and which also have a positive ecological impact;
- the aspect of the lab samples shows that there is a large quantity of vitreous mass surrounding the alite and belite crystals, which determines the clinker hydrating process to slow down and a reduction of the mechanical strength of the resulting hardened cement.

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